

Field volatility of Dicamba DGA

Report: MRID 51134103. Toth, B.N., M.R. Arpino, S.H. Bagcilar, N. Pai, A.P. Rice, D. Chase, E. Sall, L.B. Sisco, and J. Stryker. Field Volatility of Spray Solutions Containing Dicamba for Post-emergent Uses: Mon 76980 (22 oz/A) with different tank mix partners. Unpublished study performed by Stone Environmental, Inc., Montpelier, Vermont; Analytical Bio-Chemistry Laboratories, Inc., Columbia, Missouri; and AGVISE Laboratories, Northwood, North Dakota; sponsored and submitted by Monsanto Company, Chesterfield, Missouri. Stone Study ID: 18-047. Monsanto Study ID: STC-2018-0085. Reference No.: MSL0029811. Experiment initiation May 6, 2018 and completion May 9, 2018 (p. 7). Study initiation April 13, 2018 and completion September 10, 2018.

Document No.: MRID 51134103

Guideline: OCSPP 835.8100

Statements: The study was completed in compliance with U.S. EPA FIFRA GLP standards (40 CFR Part 160) with the exception of test site observations, study weather data, pesticide and crop history, soil taxonomy, and test plot preparation (p. 3). Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5, 8).

Classification: This study is **acceptable**. Monitoring started after the conclusion of application. An independent laboratory method validation was not conducted. While the study was conducted in a hot, arid region on cotton, it may not be representative of regions of more humid portions of the country where soybean is grown.


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This Data Evaluation Record may have been altered by the Environmental Fate and Effects Division subsequent to signing by CDM/CSS-Dynamac JV personnel. The CDM/CSS-Dynamac Joint Venture role does not include establishing Agency policies.

Executive Summary

Field volatilization of dicamba formulation MON 76980 when tank mixed with glyphosate potassium salt (MON 79789), potassium acetate (MON 51817), and Intact™ (polyethylene glycol, choline chloride, and guar gum) was examined from two test plots planted in dicamba-

tolerant cotton near Maricopa, Arizona. Air sampling was conducted for *ca.* 72 hours following application. Dicamba was applied to both plots at a nominal rate of 0.5 lbs. a.e./A. The treated plots were *ca.* 260 m apart. No control plot was established for field volatilization measurements. **Figures 1 and 2** depict the flux rates from the two trials.

Under field conditions at the Treatment 1 test site, based on calculations using the Indirect method, a peak volatile flux rate of $0.000045 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0015% of the applied dicamba observed 6.0 to 12 hours post-application. By the end of the study, a total of 0.0080% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

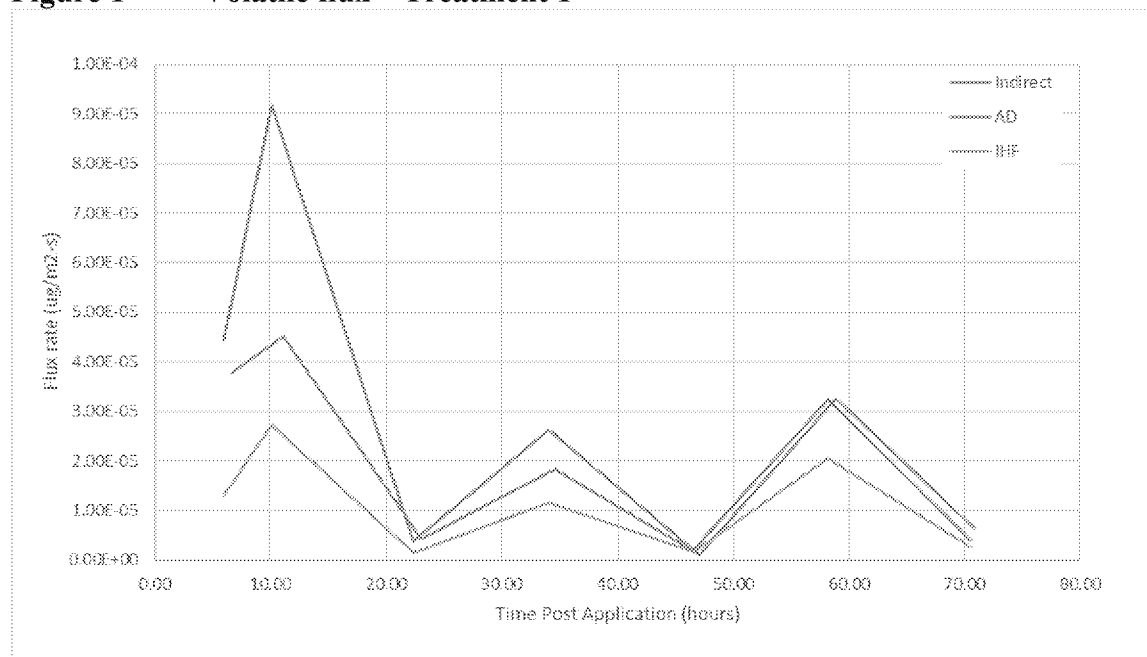
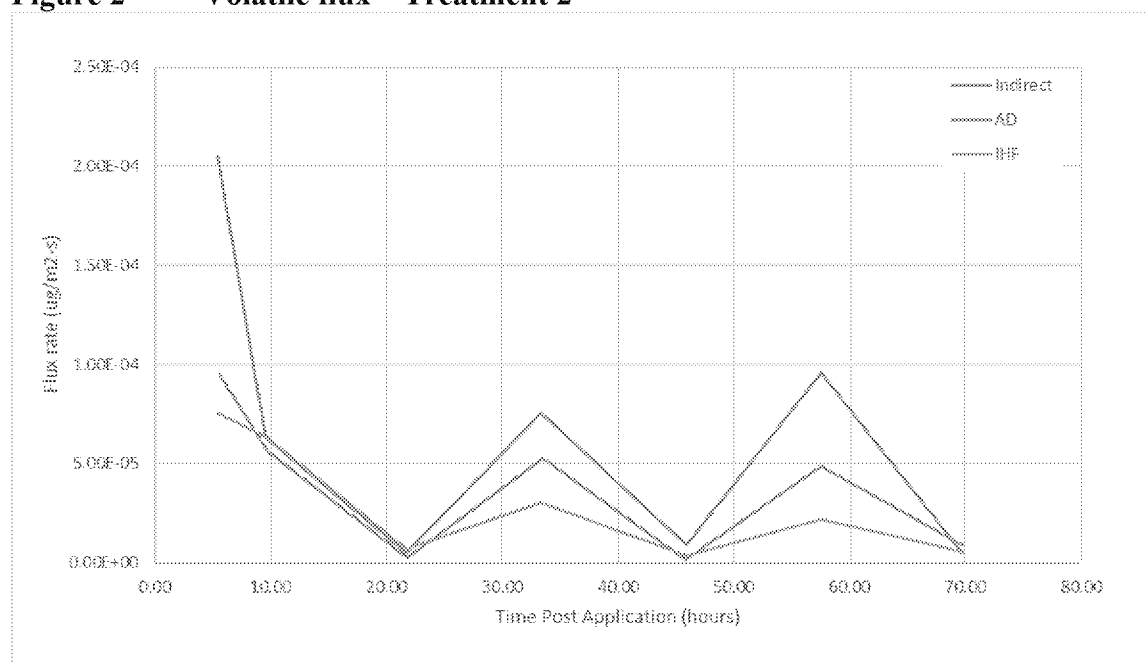
Under field conditions at the Treatment 1 test site, based on calculations using the Integrated Horizontal Flux method, a peak volatile flux rate of $0.000027 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0007% of the applied dicamba observed 6.0 to 12 hours post-application. By the end of the study, a total of 0.0041% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Under field conditions at the Treatment 1 test site, based on calculations using the Aerodynamic method, a peak volatile flux rate of $0.000092 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0016% of the applied dicamba observed 6.0 to 12 hours post-application. By the end of the study, a total of 0.0092% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Under field conditions at the Treatment 2 test site, based on calculations using the Indirect method, a peak volatile flux rate of $0.000095 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0031% of the applied dicamba observed 0 to 6 hours post-application. By the end of the study, a total of 0.0139% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Under field conditions at the Treatment 2 test site, based on calculations using the Integrated Horizontal Flux method, a peak volatile flux rate of $0.000076 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0025% of the applied dicamba observed 0 to 6 hours post-application. By the end of the study, a total of 0.0093% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Under field conditions at the Treatment 2 test site, based on calculations using the Aerodynamic method, a peak volatile flux rate of $0.000205 \mu\text{g}/\text{m}^2\cdot\text{s}$ was measured accounting for 0.0064% of the applied dicamba observed 0 to 6 hours post-application. By the end of the study, a total of 0.0224% of dicamba volatilized and was lost from the field. Peak and secondary peak volatile flux rates occurred during the warm daytime hours each day after application.

Figure 1 Volatile flux – Treatment 1**Figure 2** Volatile flux – Treatment 2

I. Materials and Methods

A. Materials

1. Test Material

Product Name: MON 76980 (diglycolamine salt of dicamba, p. 17)

Formulation Type: Liquid

CAS #: 104040-79-1

Lot Number: 11479577

Storage stability: The expiration date of the test substance was April 6, 2019.

Product Name: MON 79789 (potassium salt of glyphosate, p. 18)

Formulation Type: Liquid

CAS #: 70901-12-1

Lot Number: 11479576

Storage stability: The expiration date of the test substance was April 5, 2019.

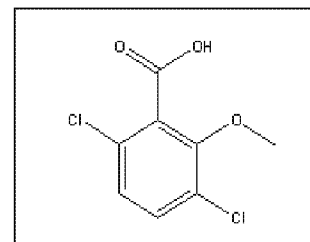
Product Name: MON 51817 (potassium acetate, p. 18)

Formulation Type: Liquid

CAS #: 127-08-2

Lot Number: Not specified

Storage stability: The expiration date of the test substance was May 6, 2021.



2. Storage Conditions

The test substance was received from Monsanto on May 1, 2018 and stored at Santa Cruz Ranch, Stanfield, Arizona (p. 17, 19). Test substance storage temperatures were within the acceptable range of 35 to 100°F. The test substance was sprayed on both plots on May 6, 2018 (pp. 27-28). The study protocol indicates the test substance would be stored under label conditions in a monitored pesticide storage area adequate to preserve stability (Appendix B, p. 327).

B. Study Design

1. Site Description

The test plots were located in Pinal County, Arizona, *ca.* 10 miles southeast of Maricopa, Arizona and *ca.* 15 miles west of Casa Grande, Arizona (p. 20). Two dicamba-tolerant cotton-cropped test plots, each measuring *ca.* 700 ft × 560 ft (213 m × 171 m, 9 A) were treated with two different mixtures containing MON 76980 (containing dicamba; p. 21). Treatment 1 consisted of MON 76980 and MON 51817 (containing potassium acetate; p. 18). Treatment 2 consisted of MON 76980, MON 79789 (containing glyphosate potassium salt), MON 51817, and Intact™ (polyethylene glycol, choline chloride, and guar gum). The two plots were separated by 840 ft (260 m). Soil characterization indicated the USDA textural class for both plots was sandy

loam (Tables 1-2, pp. 51-52). Pesticide history for the four years preceding the study indicated no recent use of dicamba (Appendix D, pp. 360-384). Crop history for the four years preceding the study indicated the plots had been planted in alfalfa and cotton. Terrain was flat with an estimated slope of *ca.* 0%. The test plots were surrounded primarily by agricultural land (Figure 3, p. 91). Residences with trees and outbuildings were located *ca.* 0.11 miles west of the center of the Treatment 1 plot. Both fields were planted with an herbicide-tolerant variety of cotton (Delta Pine 1646 B2XF) at a rate of approximately 60,000 seeds per acre on April 6th, 2018 (p. 22). The cotton crop height at the time of application was *ca.* 7.3 cm above the surface (p. 24).

2. Application Details

Application rate(s):	<p>The target application rate was 0.5 lb a.e./A or 15 GPA (pp. 42-43, 48; Tables 11-12, pp. 61-62). The application rate for the MON 51817 was approximately 1.5 lb/A (0.75 lb potassium acetate/A). For each plot, four application monitoring samples consisting of four filter paper samples each were positioned in the spray area in locations to capture various portions of the spray boom (pp. 29-30).</p> <p>The spray rate was targeted at 15 GPA (p. 27). Using the measured spray rate of the boom and the target sprayer speed, a spray rate of 15.3 GPA was achieved for all treatments. Actual average application rates based on pass times were 15.952 GPA for Treatment 1 and 15.964 GPA for Treatment 2 (Tables 11-12, pp. 61-62).</p>
Irrigation and Water Seal(s):	No irrigation or water seals were reported in the study. No rainfall was recorded during the study (p. 42).
Tarp Applications:	Tarp use was not reported in the study.
Application Equipment:	A John Deere 4630 ground sprayer equipped with an 80-ft boom was used for the spray applications (p. 27). 33 Turbo TeeJet® Induction nozzles (TTI 11006) were installed with 30-inch spacing and the boom height was set at <i>ca.</i> 20 inches above the crop canopy (7.3 cm). The sprayer had one spray tank with a volume of 600 gallons.
Equipment Calibration Procedures:	Nozzle uniformity was tested by spraying water at a pressure of 28 psi through the boom and measuring nozzle output using SpotOn® Model SC-1 sprayer calibrator devices (p. 27). Each nozzle was tested three times to determine variability. Calibration of the sprayer and nozzles established the total boom output per minute of spray to be 16.9 GPM. The forward speed of the sprayer tractor was calibrated by timing the duration required to drive a known distance of 300 ft. Speed verification was repeated three times.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**.

Table 1. Summary of application methods and rates for dicamba

Field	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied ¹ (lbs)	Area Treated (acres)	Calculated Application Rate (lb ae/acre)	Reported Application Rate (gal/acre)
Treatment 1	Spray	5/6/2018 at 8:46	4.79	9.00	0.532	15.952
Treatment 2	Spray	5/6/2018 at 9:49	4.79	9.00	0.532	15.964

Data obtained from pp. 28-29 and Tables 11-12, pp. 61-62 of the study report.

¹ Reviewer calculated as calculated application rate (lb a.e./acre) × area treated (acres).

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

Table 2. Summary of dicamba application and monitoring schedule

Field	Treated Acres	Application Period	Initial Air/Flux Monitoring Period ¹	Water Sealing Period	Tarp Covering Period
Treatment 1	9.00	5/6/2018 between 8:46 – 8:57	5/6/2018 between 9:05 – 15:23	Not Applicable	Not Applicable
Treatment 2	9.00	5/6/2018 between 9:49 – 10:03	5/6/2018 between 10:15 – 15:22	Not Applicable	Not Applicable

Data obtained from pp. 28-29 and Tables 13-14, pp. 63-64 of the study report.

¹ Initial air monitoring periods are those for perimeter stations. The initial period at the center station for Treatment 1 was 5/6/2018 between 9:12 – 14:43 and for Treatment 2 was 5/6/2018 between 10:18 – 15:11.

3. Soil Properties

Soil properties measured before the study are provided in **Table 3**. pH of the soil was 8.2 (Tables 1-2, pp. 51-52).

Table 3. Summary of soil properties for the cotton plots

Field	Sampling Depth (inches)	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm ³)	Soil Composition
Treatment 1	0-6	Sandy Loam	Denure sandy loam	Not Reported	1.29	% Organic Carbon ¹ = 0.38% % Sand = 74% % Silt = 12% % Clay = 14%
Treatment 2	0-6	Sandy Loam	Denure sandy loam, Mohall sandy loam, and Trix clay loam	Not Reported	1.26	% Organic Carbon ¹ = 0.48% % Sand = 72% % Silt = 12% % Clay = 16%

Data obtained from pp. 24-25; Tables 1-2, pp. 51-52; and Appendix E, pp. 394-396 of the study report.

¹Reviewer calculated as: organic carbon (%) = organic matter (%) / 1.72. Organic matter was reported as 0.65% in the Treatment 1 plot and 0.82% in the Treatment 2 plot.

During application for Treatment 1, the maximum soil temperatures at the surface, 2" depth, and 6" depth were 98.1°F (36.7°C), 69.8°F (21.0°C), and 70.4°F (21.3°C), respectively (Table 4, p. 54). Maximum soil moisture at 2" depth was 0.2056 m³/m³. During application for Treatment 2, the maximum soil temperatures at the surface, 2" depth, and 6" depth were 103.8°F (39.9°C), 73.4°F (23.0°C), and 70.7°F (21.5°C), respectively (Table 7, p. 57). Maximum soil moisture at 2" depth was 0.3705 m³/m³. Hourly soil temperature and soil moisture data were not reported.

4. Source Water

Tank mix water was obtained on May 5, 2018 (well water). The field pH of the source water was 8.0. The pH of the tank mix water was 7.9 with a hardness of 909 mg CaCO₃/L and a conductivity of 2.48 mmhos/cm (pp. 53).

5. Meteorological Sampling

Site meteorological stations were positioned *ca.* 1.0 miles and 0.7 miles east of the Treatment 1 and 2 plots, respectively (pp. 25-26). The system included an Onset Computer Corporation HOBO[®] RX3000 Remote Monitoring Station data logger with attached Onset Computer Corporation HOBO[®] Smart Sensors for monitoring precipitation (1.3 m above the ground), air temperature and relative humidity (1.6, 4.8, and 9.4 m above the ground), soil temperature (at depths of 1 mm, 2 inches, and 6 inches), soil moisture (2 inch depth), and solar radiation (2.4 m above the ground). These parameters were measured at one-minute intervals with the exception of a *ca.* four-hour period when the meteorological station was being moved. Additionally, the station included a Campbell Scientific CR6 data logger with attached sensors for measuring wind speed and direction at 1.7, 5.0, and 10.3 m above the ground surface. These parameters were measured at one-second intervals except for the four-hour period during which the station was moved.

An additional soil sensor station was located in the same field as the two treatment plots (p. 26). This station consisted of an Onset HOBO[®] Microstation with sensors for measuring soil moisture (2-inch depth) and soil temperature (depths of 1 mm, 2 inches, and 6 inches).

Flux meteorological stations were deployed near each test plot *ca.* 5 m from the application area (p. 26). The flux monitoring stations used Gill Instruments WindSonic Option 3 (1405-PK-040) 2-dimensional sonic anemometers to measure wind speed and wind direction at heights of 0.33, 0.55, 0.90, and 1.5 m above the crop surface. Data were recorded on a Campbell Scientific CR6 Series data logger. An Onset S-THB-M008 smart sensor was used to measure air temperature and relative humidity at the same four heights. Air temperature and humidity data were recorded on an Onset HOBO® Microstation data logger. Wind speed, wind direction, and temperature data were one-minute data (Table 5, p. 55 and Table 8, p. 58).

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in **Table 4**. The location of the meteorological equipment is shown in **Attachment 3**.

Table 4. Summary of meteorological parameters measured in the field

Meteorological Station	Minimum Fetch (m)	Parameter	Monitoring heights (m)	Averaging Period
Site Met. Station	Not Reported	Air temperature	1.6, 4.8, and 9.4	1 minute
		Relative humidity	1.6, 4.8, and 9.4	1 minute
		Wind speed/wind direction	1.7, 5.0, and 10.3	1 second
		Solar radiation	2.4	1 minute
		Precipitation	1.3	1 minute
		Soil temperature	1 mm, 2 in., and 6 in. depth	1 minute
		Soil moisture	2 inch depth	1 minute
Soil Sensor Station	Not Reported	Soil temperature	1 mm, 2 in., and 6 in. depth	Not Reported
		Soil moisture	2 inch depth	Not Reported
Treatment 1 Flux Met. Station	102.55	Air temperature	0.33, 0.55, 0.90, and 1.5*	1 minute
		Relative humidity	0.33, 0.55, 0.90, and 1.5*	Not Reported
		Wind speed/wind direction	0.33, 0.55, 0.90, and 1.5*	1 minute
Treatment 2 Flux Met. Station	103.20	Air temperature	0.33, 0.55, 0.90, and 1.5*	1 minute
		Relative humidity	0.33, 0.55, 0.90, and 1.5*	Not Reported
		Wind speed/wind direction	0.33, 0.55, 0.90, and 1.5*	1 minute

Data obtained from pp. 25-26; Table 5, p. 55; Table 8, p. 58; and Appendix H, pp. 418-419 of the study report.

* Height reflects height above the crop canopy.

6. Air Sampling

Two pre-application samples were collected at 0.15 m above the crop canopy at the approximate center of each test plot (p. 29). Samples were collected for *ca.* 6 hours from afternoon to early evening on May 5, 2018.

Post-application in-field air samplers were used for flux monitoring for *ca.* 72 hours following application at both test plots (pp. 30-31). Samplers were placed on a mast in the approximate center of each plot directly following spray application at heights of 0.15, 0.33, 0.55, 0.90, and 1.5 m above the crop canopy. Samples were collected at *ca.* 6, 12, 24, 36, 48, 60, and 72 hours post-application. The 0 to 6-hour and 6 to 12-hour samples were pro-rated based on the time remaining until sunset on the day of application, with subsequent samples being collected on a sunrise-sunset schedule.

Off the plots, eight perimeter air monitoring stations were located 1.5 m above the crop canopy and 5 m outside the edge of each plot (pp. 30-31). Samples were collected at *ca.* 6, 12, 24, 36, 48, 60, and 72 hours post-application. The sampling schedule was the same as for the in-field air sampling.

7. Sample Handling and Storage Stability

PUF sorbent tube samples were handled with nitrile gloves (p. 32). PUF sorbent tubes were placed in pre-labeled conical tubes. All PUF samples were stored in coolers containing dry ice or chest freezers prior to shipment and were shipped in coolers containing dry ice to the analytical testing facility. Pre-application, during application, post-application, spray area, field exposed spikes, and transit samples were stored in a chest freezer or in coolers containing dry ice and shipped in coolers containing dry ice until final transfer to storage at -20 °C prior to laboratory analysis. Tank mix samples were stored and shipped under ambient conditions. Samples were shipped by overnight FedEx to EAG Laboratories, Columbia, Missouri.

All field collected PUF samples were extracted within 11 days after collection (Appendix A, pp. 121-122). All field exposed QC and transit stability samples were extracted within 14 days after fortification. All samples were analyzed within 1 day of extraction. Stability of dicamba was demonstrated for at least 78 days during frozen storage in a stability study (Maher 2016). All PUF samples were analyzed within the demonstrated stability.

8. Analytical Methodology

- **Sampling Procedure and Trapping Material:** Flux monitoring equipment for the center masts consisted of PUF sorbent tubes housed in ¾ inch diameter PVC pipes (p. 23). SKC AirChek 52 air sampling pumps were used, covered with plastic bags to protect them from precipitation. Pumps were calibrated to a flow rate of 2.950-3.050 L/min (p. 24). For perimeter flux monitoring, single air samplers were positioned outside the perimeter with the sorbent tube openings oriented away from the plot and the air inlet at a height of *ca.* 1.5 m above the crop surface.
- **Extraction method:** The contents of the PUF sorbent tubes were extracted using methanol containing stable-labelled internal standard (Appendix A, Appendix D, pp. 161-184). The sample was fortified with internal standard, a grinding ball was added to the tube, and 29.8 mL of methanol was added. The sample tubes were capped and agitated on a high-speed shaker (Geno/Grinder®) for 1200 cycles per minute for 30 minutes. The cap was removed, and a 1.5 mL aliquot was transferred to a 0.45 µm polypropylene 96-well filter plate with a clean polypropylene plate positioned below the filter plate (Appendix A, Appendix D, pp. 185-186). The sample was evaporated to dryness under nitrogen at 50°C. The sample was reconstituted with 0.150 mL of 25% methanol in water. The sample was mixed and analyzed by LC-MS/MS with electrospray ionization in negative ion mode within the storage time determined during method validation (Appendix A, p. 121).
- **Method validation (Including LOD and LOQ):** Method validation was achieved by fortifying 18 replicate fortification samples at each of three fortification levels (0.3 ng/PUF, 3 ng/PUF,

and 60 ng/PUF; Appendix A, Appendix D, pp. 179-183). Validation assessments showed acceptable accuracy between 70% and 120% and precision ($<20\%$ RSD) for all fortified matrices at each fortification level for both primary and secondary ion transitions. Average recoveries for primary ion transitions were 89%, 94%, and 90% at 0.3, 3, and 60 ng/PUF, respectively. Average recoveries for secondary ion transitions were 93%, 97%, and 98% at 0.3, 3, and 60 ng/PUF, respectively. No independent laboratory validation is provided. For primary ion transitions, the LOQ during method validation was 0.30 ng/PUF and the LOD was 0.094 ng/PUF (Appendix A, Appendix D, p. 180). For secondary ion transitions, the LOQ during method validation was 0.30 ng/PUF and the LOD was 0.065 ng/PUF. During the study, the LOQ was 1.0 ng/PUF (p. 32).

- Instrument performance: Calibration standards were prepared at concentrations ranging from 0.15 to 75 ng/PUF (Appendix A, Appendix D, p. 167). Concentrations were 0.15, 0.225, 0.3, 0.75, 1.5, 2.25, 3, 7.5, 15, 22.5, 30, and 75 ng/PUF. Analyst[®] software was used to derive the calibration curve using a weighted linear curve (1/x; Appendix A, Appendix D, pp. 173 and Appendix A, Appendix G, p. 209).

9. Quality Control for Air Sampling

Lab Recovery: 15 of 24 laboratory spike recoveries are within the acceptable range of 90-110% (Appendix A, Appendix G, pp. 212-213). All laboratory spike recoveries are within the range of 74-104%. Laboratory spike samples were prepared at fortification levels of 1 ng/PUF (12 samples) and 60 ng/PUF (12 samples). Average recoveries were 85% and 101% at 1 ng/PUF and 60 ng/PUF, respectively.

Field blanks: Two pre-application samples were collected from the center of each test plot for *ca.* 6 hours from early afternoon to evening on May 5, 2018 (p. 29). Dicamba was not detected in the four pre-application samples (Table 19, p. 69 and Table 21, p. 72).

All eight control samples from field spike analyses also contained no detectable dicamba (Appendix A, Appendix G, pp. 212-213).

Field Recovery: Twelve 6-hour and twelve 12-hour field spike samples were collected at concentration levels of 0, 3, 10, and 60 ng/PUF (p. 31). A total of six field spikes were prepared at each concentration level. Most field spike recoveries are within the acceptable range with overall recoveries of 86% to 89% at 3 ng/PUF, 93% to 99% at 10 ng/PUF, and 92% to 102% at 60 ng/PUF.

Travel Recovery: Three transit stability PUF samples were fortified at 10 ng/PUF and placed on dry ice along with three unfortified control samples (pp. 31-32). Dicamba was not detected in any of the three control samples (Appendix A, Appendix G, p. 224). The range of recoveries from the fortified samples was from 93% to 97% (p. 41).

Breakthrough: Laboratory spike samples that were fortified at 60 ng/PUF had recoveries ranging from 98% to 104% (Appendix A, Appendix G, pp. 212-213). The highest dicamba amount measured on a PUF sample (excluding laboratory and field spikes) was 2.95 ng/PUF (Appendix A, Appendix G, pp. 216-223) which is *ca.* 5% of the highest fortification level, indicating that dicamba loss due to breakthrough is unlikely.

10. Application Verification

Four application monitoring sampling stations, each consisting of four 12.5 cm diameter Whatman #3 filter paper samples, were positioned in the spray area at crop height on each plot (pp. 19, 29-30). The stations were positioned to capture different portions of the spray boom and different spray nozzles. The average recovery relative to the target was 98.5% for Treatment 1 and 94.1% for Treatment 2 (p. 43).

Actual spray application rates were determined using swath pass times, the dimensions of the spray swaths, the target application rate, and the calibrated total boom output (pp. 42-43). Calculated actual application rates were compared to the target application rate of 15 GPA. The average percent of target dicamba applied was 106% for both Treatment 1 and Treatment 2.

Tank mix samples were also collected and analyzed to verify the amount of dicamba present in the tank mix (p. 41). The theoretical tank mix concentration was 0.40% dicamba. Tank mix samples indicated an actual tank mix concentration of 0.378% dicamba for Treatment 1 and 0.368% dicamba for Treatment 2.

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

Indirect Method

The indirect method, commonly referred to as the “back calculation” method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the indirect method, air samples are collected at various locations outside the boundaries of a treated field. Meteorological conditions, including air temperature, wind speed, and wind direction, are also collected for the duration of the sampling event. The dimensions and orientation of the treated field, the location of the samplers, and the meteorological information are used in combination with the AERMOD dispersion model (Version 18081) and a unit flux rate of 0.001 g/m²s to estimate concentrations at the sampler locations. Since there is a linear relationship between flux and the concentration at a given location, the results from the AERMOD model runs are compared to those concentrations actually measured, and a regression is performed, using the modeled values along the x-axis and the measured values along the y-axis. If the linear regression does not result in a statistically significant relationship, the regression may be rerun forcing the intercept through the origin, or the ratio of averages between the monitored to modeled

concentrations may be computed, removing the spatial relationship of the concentrations. The indirect method flux back calculation procedure is described in detail in Johnson et al., 1999.

Study authors used a similar analysis to obtain flux rates. However, if, after regression analysis, the linear regression did not result in a statistically significant relationship, instead of rerunning the regression by forcing the intercept through zero, the spatial relationship was removed by sorting both the measured and modeled air concentrations (independently) in ascending order, then redoing the regression, with the final flux estimate calculated as the slope of this alternative regression multiplied by the nominal flux. If the sorted regression was also not statistically significant, the ratio of the sum of the measured concentrations to the sum of the modeled concentrations was multiplied by the nominal flux to get the final flux estimate.

Aerodynamic Method

The aerodynamic method, also referred to as the “flux-gradient” method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the aerodynamic method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from 0.5 to 10 feet. Likewise, temperature and wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method is Thornthwaite-Holzman Equation, Equation 1, which is shown in the following expression:

$$\text{Equation 1} \quad P = \frac{k^2 (\Delta \bar{c})(\Delta \bar{u})}{\phi_m \phi_p \left[\ln \left(\frac{z_2}{z_1} \right) \right]^2}$$

where P is the flux in units of $\mu\text{g}/\text{m}^2 \cdot \text{s}$, k is the von Karman's constant (dimensionless ~ 0.4), $\Delta \bar{c}$ is the vertical gradient pesticide residue concentration in air in units of $\mu\text{g}/\text{m}^3$ between heights z_{top} and z_{bottom} in units of meters, $\Delta \bar{u}$ is the vertical gradient wind speed in units of m/s between heights z_{top} and z_{bottom} , and ϕ_m and ϕ_p are the momentum and vapor stability correction terms respectively. Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression is incorporated into Equation 1 to arrive at Equation 2 which is ultimately used to compute the flux.

$$\text{Equation 2} \quad \text{Flux} = \frac{-(0.42)^2 (c_{z_{\text{top}}} - c_{z_{\text{bottom}}})(u_{z_{\text{top}}} - u_{z_{\text{bottom}}})}{\phi_m \phi_p \ln \left(\frac{z_{\text{top}}}{z_{\text{bottom}}} \right)^2}$$

where ϕ_m and ϕ_p are internal boundary layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i :

$$\text{Equation x3} \quad R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2} \right) + 273.16 \right] + (u_{ztop} - u_{zbottom})^2}$$

where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if $R_i > 0$ (for Stagnant/Stable IBL)

$$\phi_m = (1 + 16R_i)^{0.33} \text{ and } \phi_p = 0.885(1 + 34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)

$$\phi_m = (1 - 16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1 - 22R_i)^{-0.4}$$

The minimum fetch requirement, that the fetch be 100 times the highest height of the air sampler for this method to be valid, was not satisfied for any of the sampling periods. Given the highest height sampled was 1.57 m (1.5 m above the crop which was 7.3 cm), the minimum fetch distance is 157 m. The maximum fetch during the conduct of the study was 112 m, which is about 29% below the minimum fetch requirement. As such, there is some uncertainty in the flux rates derived from this analysis, as the internal boundary layer depth may not have been sufficient. The aerodynamic method used to estimate flux and related equations are presented in Majewski et al., 1990.

Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the “mass balance” method, was the technique employed for estimating flux rates from fields treated for this field study given the available data. In the integrated horizontal flux method, a mast is erected in the middle of the treated field and concentration samples are typically collected at four or five different heights, ranging from approximately 0.5 to 5 feet. Likewise, wind speed data are collected at a variety of heights. A log-linear regression is performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log law relationships for the atmospheric boundary layer. These relationships are then incorporated into an equation to estimate flux. The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux method is the following expression:

$$\text{Equation 3} \quad P = \frac{1}{x} \int_{Z_0}^{Z_p} \bar{c} \bar{u} dz$$

where P is the volatile flux in units of $\mu\text{g}/\text{m}^2 \cdot \text{s}$, \bar{c} is the average pesticide residue concentration in units of $\mu\text{g}/\text{m}^3$ at height Z in units of meters, \bar{u} is the wind speed in units of m/s at height Z , x

is the fetch of the air trajectory blowing across the field in units of meters, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top in units of meters, and dz is the depth of an incremental layer in units of meters. Following trapezoidal integration, equation 3 is simplified as follows in equation 4 (Yates, 1996):

$$\text{Equation 4} \quad P = \frac{1}{x} \sum_{Z_0}^{Z_p} (A * \ln(z) + B) * (C * \ln(z) + D) dz$$

where A is the slope of the wind speed regression line by $\ln(z)$, B is the intercept of the wind speed regression line by $\ln(z)$, C is the slope of the concentration regression by $\ln(z)$, D is the intercept of the concentration regression by $\ln(z)$, z is the height above ground level. Z_p can be determined from the following equation:

$$\text{Equation 5} \quad Z_p = \exp\left[\frac{(0.1 - D)}{C}\right]$$

The minimum fetch requirement (20 meters) for this method to be valid was satisfied at all times. The surface characteristics of the field consisted of soybeans at a height of 7.3 cm. The surface roughness length ranged from 0.00002 - 0.05 m, below the required of 0.1 meters for this method to be valid.

B. Temporal Flux Profile

The flux determined from the registrant and reviewer for each sampling period after the application is provided in **Tables 5 through 8**. It should be noted that meteorological data were unavailable for using in modeling concentrations for use in the indirect method, so the reviewer relied on those modeled concentrations provided in the study.

Table 5. Field volatilization flux rates of dicamba for Treatment 1 – Indirect Method

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes
1	5/6/18 9:05 – 15:23	6:18	0.000038	Regression	0.000038	A
2	5/6/18 14:45 – 19:51	5:06	0.000045	Ratio of averages	0.000058	B
3	5/6/18-5/7/18 18:50 – 7:49	12:59	0.000004	Regression	0.000006	B
4	5/7/18 7:06 – 19:20	12:14	0.000018	Regression no intercept	0.000026	B
5	5/7/18-5/8/18 18:46 – 7:49	13:03	0.000001	Regression no intercept	0.000003	B
6	5/8/18 7:06 – 19:38	12:32	0.000033	Regression no intercept	0.000030	B

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes
7	5/8/18-5/9/18 18:55 – 7:36	12:41	0.000006	Regression no intercept	0.000011	C

Data obtained from Table 13, p. 63 and Table 24, p. 78 of the study report.

Notes

- A The spatial regression method was used to calculate the flux estimate for the sampling period.
 B The sorted regression method was used to calculate the flux estimate for the sampling period.
 C The ratio method was used to calculate the flux estimate for the sampling period.

Table 6. Field volatilization flux rates of dicamba for Treatment 1 – Integrated Horizontal Flux and Aerodynamic Methods

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Empirical Flux Determination Method*	Notes
1	5/6/18 9:12 – 14:43	5:31	0.000013	0.000015	IHF	
			0.000044	0.000030	AD	
2	5/6/18 14:45 – 18:54	4:09	0.000027	0.000025	IHF	
			0.000092	0.000071	AD	
3	5/6/18-5/7/18 18:56 – 7:06	12:10	0.000002	0.000001	IHF	
			0.000004	0.000003	AD	
4	5/7/18 7:07 – 18:47	11:40	0.000012	0.000012	IHF	
			0.000026	0.000019	AD	
5	5/7/18-5/8/18 18:48 – 7:17	12:29	0.000002	0.000002	IHF	
			0.000002	0.000002	AD	
6	5/8/18 7:18 – 18:56	11:38	0.000021	0.000023	IHF	
			0.000032	0.000023	AD	
7	5/8/18-5/9/18 18:57 – 7:17	12:20	0.000003	0.000003	IHF	
			0.000004	0.000003	AD	

Data obtained from Table 13, p. 63; Appendix H, p. 418; and Appendix I, p. 422 of the study report.

*Methods legend: AD = Aerodynamic Method, IHF = Integrated Horizontal Flux.

Table 7. Field volatilization flux rates of dicamba for Treatment 2 – Indirect Method

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes
1	5/6/18 10:15 – 15:22	5:07	0.000095	Regression	0.000095	A
2	5/6/18 14:44 – 19:30	4:46	0.000056	Regression	0.000056	A
3	5/6/18-5/7/18 18:50 – 7:34	12:44	0.000003	Regression	0.000004	B
4	5/7/18 7:03 – 19:17	12:14	0.000053	Regression	0.000053	A

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Notes
5	5/7/18-5/8/18 18:45 – 7:40	12:55	0.000001	Regression no intercept	0.000004	B
6	5/8/18 7:04 – 19:22	12:18	0.000049	Regression	0.000049	A
7	5/8/18-5/9/18 18:54 – 7:31	12:37	0.000009	Regression no intercept	0.000006	B

Data obtained from Table 14, p. 64 and Table 27, p. 83 of the study report.

Notes

- A The spatial regression method was used to calculate the flux estimate for the sampling period.
 B The sorted regression method was used to calculate the flux estimate for the sampling period.

Table 8. Field volatilization flux rates of dicamba for Treatment 2 – Integrated Horizontal Flux and Aerodynamic Methods

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			Reviewer ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Registrant ($\mu\text{g}/\text{m}^2\cdot\text{s}$)	Empirical Flux Determination Method*	Notes
1	5/6/18 10:18 – 15:11	4:53	0.000076 0.000205	0.000081 0.000146	IHF AD	
2	5/6/18 15:15 – 19:23	4:08	0.000064 0.000063	0.000068 0.000048	IHF AD	
3	5/6/18-5/7/18 19:24 – 7:29	12:05	0.000007 0.000005	0.000007 0.000004	IHF AD	
4	5/7/18 7:31 – 19:11	11:40	0.000030 0.000076	0.000032 0.000055	IHF AD	
5	5/7/18-5/8/18 19:13 – 7:43	12:30	0.000004 0.000009	0.000003 0.000007	IHF AD	
6	5/8/18 7:44 – 19:22	11:38	0.000022 0.000096	0.000022 0.000070	IHF AD	
7	5/8/18-5/9/18 19:25 – 7:35	12:10	0.000006 0.000004	0.000006 0.000003	IHF AD	

Data obtained from Table 14, p. 64; Appendix H, p. 419; and Appendix I, p. 424 of the study report.

*Methods legend: AD = Aerodynamic Method, IHF = Integrated Horizontal Flux.

For Treatment 1, the maximum flux rate calculated by all three methods occurred during the second sampling period after application. The maximum flux rates were $0.000045 \mu\text{g}/\text{m}^2\cdot\text{s}$, $0.000027 \mu\text{g}/\text{m}^2\cdot\text{s}$, and $0.000092 \mu\text{g}/\text{m}^2\cdot\text{s}$ as calculated by the indirect, integrated horizontal flux, and aerodynamic methods, respectively. Flux rates were higher during the warm daytime hours each day and lower during the cooler overnight hours.

For Treatment 1, R-squared values for the linear regressions of modeled and measured air concentrations in the indirect method ranged from 0.22 to 0.81. Linear regression was used to

estimate flux during periods 1 and 3. The regression with no intercept method was used for periods 4 through 7. The ratio method was used to estimate flux during period 2.

R-squared values in log-linear vertical profiles of wind speed for Treatment 1 were generally high with all R-squared values ≥ 0.92 . R-squared values in log-linear vertical profiles of concentration ranged from 0.75 to 0.95. R-squared values in log-linear vertical profiles of temperature ranged from 0.94 to >0.99 .

For Treatment 2, the maximum flux rate calculated by all three methods occurred during the first sampling period after application. The maximum flux rates were $0.000095 \mu\text{g}/\text{m}^2\cdot\text{s}$, $0.000076 \mu\text{g}/\text{m}^2\cdot\text{s}$, and $0.000205 \mu\text{g}/\text{m}^2\cdot\text{s}$ as calculated by the indirect, integrated horizontal flux, and aerodynamic methods, respectively. Flux rates were higher during the warm daytime hours each day and lower during the cooler overnight hours.

For Treatment 2, R-squared values for the linear regressions of modeled and measured air concentrations in the indirect method ranged from 0.13 to 0.84 (Table 27, p. 83). R-squared values were <0.70 for periods 2 (0.50), 3 (0.25), 4 (0.62), 5 (0.13), and 7 (0.64). Spatial regression was used to estimate flux during periods 1 through 4 and 6. The regression with no intercept method was used for periods 5 and 7.

R-squared values in log-linear vertical profiles of wind speed for Treatment 2 were generally high with all R-squared values ≥ 0.97 . R-squared values in log-linear vertical profiles of concentration ranged from 0.68 to 0.99. R-squared values in log-linear vertical profiles of temperature were > 0.98 .

III. Study Deficiencies and Reviewer's Comments

1. Soil temperature and moisture data are not reported on an hourly basis.
2. The registrant used a different approach to calculate Z_p , the top of the concentration plume, than that recommended by EPA when calculating volatilization flux rates using the Integrated Horizontal Flux method (p. 37). The registrant used:

$$Z_p = \exp\left(\frac{-D}{C}\right)$$

C and D are the slope and intercept of the log-linear concentration regression. The 0.1 term in EPA's equation was removed. The 0.1 represents the concentration at the top of the plume, which is a carryover from the use of this technique for estimating flux rates for fumigants, which typically have much higher concentrations than those anticipated for semi-volatile chemicals like dicamba. The revised equation is acceptable to the reviewer and does not significantly impact the estimate of flux rates.

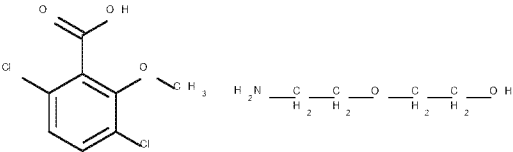
3. The total percent of applied mass lost for the indirect method incorrectly excludes Period 7 from the calculation (Table 25, p. 79, and Table 28, p. 84).

4. Percent of applied mass lost is based on the actual application rate for the indirect method (pp. 46-47) and the target application rate for the integrated horizontal flux and aerodynamic methods (p. 48).
5. The study was conducted in compliance with U.S. EPA Good Laboratory Practice requirements with exceptions related to test site observations, study weather data, pesticide and crop history, soil taxonomy, and test plot preparation prior to application (p. 3).
6. The first air monitoring period started after the conclusion of application.
7. Analytical method validation was performed, but the method was not independently validated. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.
8. Soil was characterized and a USDA soil resource report was included in the study (Appendix E, pp. 385-403), but no WRB soil taxonomic classification was provided.
9. Soil bulk density and organic matter content were reported in composite samples from both plots but at only a single depth of 0-6 inches.

IV. References

- Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California, Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.
- Maher, D. 2016. Storage Stability of Dicamba on Polyurethane Foam Air Sampling Traps. Monsanto Technical Report MSL0026782. St. Louis, Missouri.
- Majewski, M.S., Glotfely, D.E., Paw, K.T., and Seiber, J.N. 1990. A field comparison of several methods for measuring pesticide evaporation rates from Soil. *Environmental Science and Technology*, 24(10):1490-1497.
- Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. *Agriculture Forest Meteor.* Vol 57:281-295.
- Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," *Journal of Environmental Quality*, 25: 192-202.

Attachment 1: Chemical Names and StructuresDicamba-diglycolamine and Its Environmental Transformation Products. ^A

Code Name/ Synonym	Chemical Name	Chemical Structure	Study Type	MRID	Maximum %AR (day)	Final %AR (study length)
PARENT						
Dicamba-diglycolamine (Diglycolamine salt of dicamba)	IUPAC: 3,6-Dichloro-o-anisic acid-2-(2-aminoethoxy)ethanol CAS: 2-(2-Aminoethoxy)ethanol;3,6-dichloro-2-methoxy-benzoic acid CAS No.: 104040-79-1 Formula: C ₁₂ H ₁₇ Cl ₂ NO ₅ MW: 326.17 g/mol SMILES: COc1c(Cl)ccc(Cl)c1C(=O)O.NC COCCO		835.8100 Field volatility	51134103	NA	NA
MAJOR (>10%) TRANSFORMATION PRODUCTS						
No major transformation products were identified.						
MINOR (<10%) TRANSFORMATION PRODUCTS						
No minor transformation products were identified.						
REFERENCE COMPOUNDS NOT IDENTIFIED						
All compounds used as reference compounds were identified.						

^A AR means “applied radioactivity”. MW means “molecular weight”. NA means “not applicable”.

Attachment 2: Statistics Spreadsheets and Graphs

Supporting spreadsheet files accompany the review.

1. Air sampling periods and field spike recoveries



128931_51134103_DE
R-FATE_835.8100_9-15

2. Validation spreadsheets for the Indirect Method



128931_51134103_DE 128931_51134103_DE
R-FATE_835.8100_9-15 R-FATE_835.8100_9-15

3. Validation spreadsheets for the Integrated Horizontal Flux Method:



128931_51134103_DE 128931_51134103_DE
R-FATE_835.8100_9-15 R-FATE_835.8100_9-15

4. Validation spreadsheets for the Aerodynamic Method:



128931_51134103_DE 128931_51134103_DE
R-FATE_835.8100_9-15 R-FATE_835.8100_9-15

Attachment 3: Field Volatility Study Design and Plot Map

